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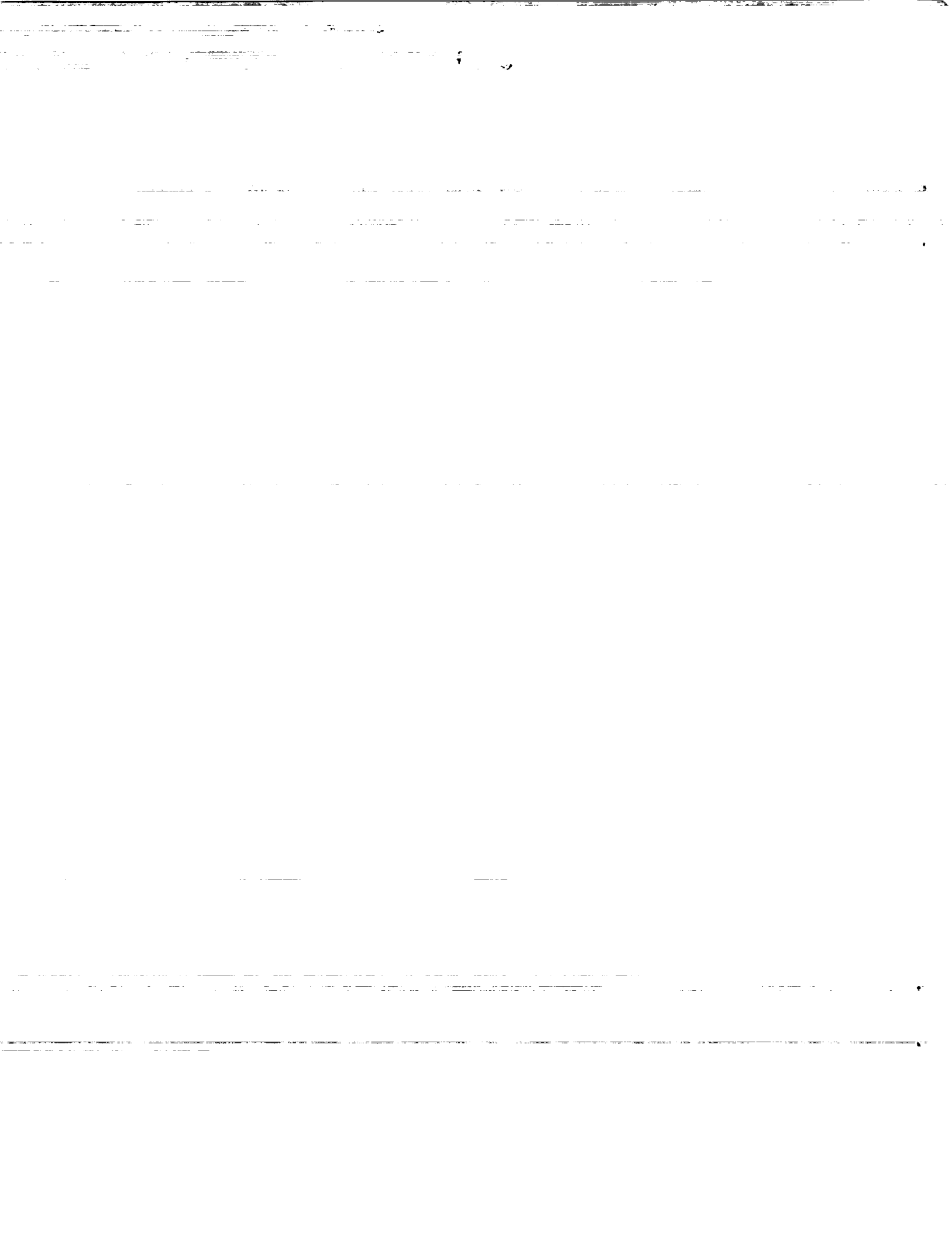
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PHYSICAL AND CHEMICAL PROPERTIES OF SOME NEW PERFLUOROPOLYALKYLETHER LUBRICANTS PREPARED BY DIRECT FLUORINATION

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SUMMARY

A series of perfluoropolyalkylether (PFPAE) fluids was synthesized by direct fluorination. Viscosity-temperature properties, oxidation stabilities, oxidation-corrosion properties, bulk modulus, lubricity, surface tension and density were measured. It was shown that as the carbon to oxygen ratio in the polymer repeating unit decreases, the viscometric properties improve, the fluids may become poorer boundary lubricants, the bulk modulus increases, the surface tension increases and the fluid density increases. The presence of difluoromethylene oxide units in the polymer does not significantly lower the oxidation and oxidation-corrosion stabilities as long as the difluoromethylene oxide units are separated by other units.

INTRODUCTION

Perfluoropolyalkylethers (PFPAE) constitute a class of fluids of which some members exhibit excellent thermal and oxidative stability (1 to 3) good viscosity-temperature characteristics (4), good elastohydrodynamic film forming capabilities (5) and are nonflammable (6). Therefore, these fluids are promising candidates for high temperature lubricant and hydraulic fluid applications. In addition, PFPAE's have been used for many years as space mechanism lubricants because of their low volatility and infrared transparency (7).

The performance of PFPAE fluids depends strongly on the molecular architecture of the polymer. Only a few commercial structures are presently available. One commercial product is prepared from hexafluoropropylene oxide (HFPO) by the anionic polymerization of HFPO monomer (Krytox fluids) (1). Another process used by another company produces PFPAE fluids by photooxidation of perfluorolefins (Fomblin Z fluids) (8). These fluids contain varying amounts of difluoromethylene oxide (formal) in the polymer chain. One of these fluids is primarily a random copolymer of difluoromethylene oxide and tetrafluoroethylene oxide.

A third PFPAE fluid is produced by polymerization of tetrafluoroacetone followed by direct fluorination (Demnum fluids) (9). This yields a fluid with a repeating unit of perfluoropropylene oxide with no branching.

However, all of these commercial fluids have one or more deficiencies. These deficiencies include: incompatibility with some metal alloys (10 to 12), susceptibility to Lewis acid attack (13 to 15), poor boundary lubricating behavior (14), and degradation in ionizing radiation environments (16 and 17).

The use of direct fluorination has been very successful in producing PFPAE's as well as a variety of other fluorinated compounds (18 to 20). Not only can PFPAE's often be made in a single-step reaction with much cheaper starting materials, but the process is extremely versatile, with the availability of the hydrocarbon precursor being the primary limiting factor.

The objective of this project was to synthesize a number of high molecular weight PFPAE fluids via direct fluorination. Several properties were measured which included: viscosity-temperature, oxidation stability, oxidation-corrosion stability, boundary lubrication, bulk modulus, surface tension, and density.

EXPERIMENTAL SECTION

Synthesis

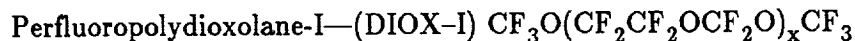
Four PFPAE fluids were synthesized. Their names, abbreviations and structures appear in table 1. The same information for the three commercial fluids appears in table 2. Complete synthesis procedures appear in reference 20. Two different direct fluorination procedures were used and are designated as "A" (21) and "B" (22). All starting materials were of research grade purity (typically, >98 percent).

Direct Fluorination Procedure A

Procedure A is fully described in reference 21. This is a variation of the La Mar direct fluorination process (18). The La Mar process involves passing fluorine, diluted with an inert gas, over the hydrocarbon ether to be fluorinated. Initially, the fluorine concentration is low (~0.5 to 10 percent) to minimize ether fragmentation. As the reaction proceeds, both the fluorine concentration and flow rate are increased until pure fluorine conditions are achieved and the ether is perfluorinated.

Fluorination procedure A (21) utilizes a hydrogen fluoride scavenger (such as NaF) which allows the use of more severe fluorination conditions (i.e., higher initial fluorine concentrations and higher flow rates). Both yield and quality of the product is improved using an HF scavenger. Nevertheless, some fragmentation still occurs which results in rearrangements leading to undesirable structures (i.e., branching) based on NMR end group analysis. In addition, this procedure also produces a product having some residual hydrogen, typically in the ppm range, based on infrared and NMR analysis.

Fluorination procedure B (22) involves the use of a perhalogenated liquid medium. The hydrocarbon ether is dissolved or dispersed in the medium and diluted fluorine is then introduced. This procedure typically produces products in higher yield and higher purity (i.e., less branching and less residual hydrogen) than procedure A or other fluorination processes. In fact, the mild conditions employed in procedure B allows chemical functionality to be retained on the fluorinated molecules.



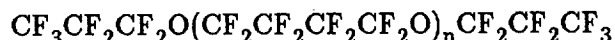
A polymerized sample of 1,3 dioxolane was directly fluorinated (A) to produce the above nominal structure. However, as mentioned above, this direct fluorination procedure (A) does produce some branching and residual hydrogen. The product was distilled to yield the following fractions:

<u>Fraction</u>	<u>Percent of Total</u>	<u>b.p. range (°C)</u>
101	21	<200 @ 1.3×10^4 Pa
102	26	>200 @ 1.3×10^4 Pa <245 @ 1.3×10^3 Pa
103	19	>245 @ 1.3×10^3 Pa <288 @ 13 Pa
104	11	>288 @ 13 Pa <340 @ 6.7 Pa
105	23	>340 @ 6.7 Pa

The physical properties of the various fractions of DIOX-I appear in table 3.

Perfluoropolydioxolane-II—(DIOX-II) $\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{OCF}_2\text{O})_x\text{CF}_3$

The nominal structure of DIOX-II is identical to that of DIOX-I. However, DIOX-II was made using a new fluorination procedure (B) which yields a fluid which is more linear with almost no branching as shown by NMR end group analysis. However, ^{19}F NMR of this fluid did indicate a perfluoropoly(tetramethylene oxide) (PTO) impurity (~6.5 wt%) having the following structure:



This fluid (DIOX II) was not fully characterized but a fraction was utilized in the oxidation stability tests.

Perfluoropolytrioxocane-I—(TRIOX-I) $\text{CF}_3\text{O}[(\text{CF}_2\text{CF}_2\text{O})_2\text{CF}_2\text{O}]_x\text{CF}_3$

The hydrocarbon polymer for this fluid was prepared from diethylene glycol and paraformaldehyde. Direct fluorination (A) and subsequent distillation yielded the following fractions:

<u>Fraction</u>	<u>Percent of Total</u>	<u>b.p. range (°C)</u>
201	26	<200 @ 1.3×10^4 Pa
202	22	>200 @ 1.3×10^4 Pa <245 @ 1.3×10^3 Pa
203	22	>245 @ 1.3×10^3 Pa <288 @ 6.7 Pa
204	19	>288 @ 6.7 Pa <370 @ 6.7 Pa
205	11	>370 @ 6.7 Pa

Physical properties of these fractions appear in table 4.

Perfluoropolytrioxocane-II—(TRIOX-II) $\text{CF}_3\text{O}[(\text{CF}_2\text{CF}_2\text{O})_2\text{CF}_2\text{O}]_x\text{CF}_3$

A sample of 1,3,6-Trioxocane was polymerized, directly fluorinated (A) and distilled to yield the following fractions:

<u>Fraction</u>	<u>Percent of Total</u>	<u>b.p. range (°C)</u>
301	31	<200 @ 1.3×10^4 Pa
302	33	>200 @ 1.3×10^4 Pa <245 @ 1.3×10^3 Pa
303	16	>245 @ 1.3×10^3 Pa <288 @ 6.7 Pa
304	10	>288 @ 6.7 Pa <370 @ 6.7 Pa
305	10	>370 @ 6.7 Pa

Physical properties appear in table 5.

Perfluoropolytrioxocane-III—(TRIOX-III) $\text{CF}_3\text{O}[(\text{CF}_2\text{CF}_2\text{O})_2\text{CF}_2\text{O}]_x\text{CF}_3$

A third sample of perfluoropolytrioxocane was prepared using the new fluorination procedure (B) which produces a more linear fluid with essentially no cross-linking or branching. However, the NMR spectrum indicated another PTO impurity (~7 wt%) in this fluid.

This is the same impurity that appeared in DIOX-II. Therefore, it was determined to be a residual product from an earlier synthesis residing in the synthesis apparatus. The impurity could not be removed by distillation because its boiling range was similar to that of the primary product. However, as will be shown later, PTO is more stable than either DIOX-II or TRIOX-III. Therefore, other than perturbing the physical properties, the presence of this impurity was not considered to invalidate the stability measurements. As with DIOX-II, TRIOX-III was not fully characterized.

Perfluoropoly(methylene oxide)—(PMO) $\text{CF}_3\text{O}(\text{CF}_2\text{O})_n\text{CF}_3$

A poly(methylene oxide) polymer was prepared by copolymerizing 1,3,5-trioxane and 1,3-dioxolane. The powder was fluorinated (A) to produce the fluid which was distilled to give the following fractions:

<u>Fraction</u>	<u>Percent of Total</u>	<u>b.p. range (°C)</u>
401	22	<210 @ 1.3×10^4 Pa
402	19	>210 @ 1.3×10^4 Pa <223 @ 2×10^3 Pa
403	20	>223 @ 2×10^3 Pa <275 @ 6.7 Pa
404	16	>275 @ 6.7 Pa <335 @ 6.7 Pa
405	23	>335 @ 6.7 Pa

The undistilled sample was analyzed by ^1H NMR and was shown to have no detectable hydrogen (i.e., $<5\text{ppm}$). The fluid was shown by ^{19}F NMR to contain 95.4 percent OCF_2O units and 4.6 percent $\text{OCF}_2\text{CF}_2\text{O}$. Properties of the various fractions appear in table 6.

Perfluoropoly(ethylene oxide)— $(\text{PEO}) \text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_x\text{CF}_3$

A 1000 MW polyethylene glycol was fluorinated (B) to yield perfluoropoly(ethylene oxide) which was distilled to give the following fractions:

<u>Fraction</u>	<u>Percent of Total</u>	<u>b.p. range ($^{\circ}\text{C}$)</u>
501	13	<200 @ 1.3×10^4 Pa
502	40	>200 @ 1.3×10^4 Pa <245 @ 1.3×10^3 Pa
503	36	>245 @ 1.3×10^3 Pa <288 @ 6.7 Pa
504	7	>288 @ 6.7 Pa <343 @ 6.7 Pa
505	4	>343 @ 6.7 Pa

Properties for these fractions appear in table 7.

Viscosity-Temperature Properties

Tables 3 to 7 contain viscosity-temperature data for all fluids (except DIOX-II and TRIOX-III). Some of the higher MW fractions have been plotted on a ASTM (D-341) temperature-viscosity chart as shown in figure 1. Figure 2 contains the ASTM slope (tables 3 to 7) plotted as a function of carbon to oxygen ratio for low, intermediate, and high viscosity fractions.

Thermal-Oxidative Behavior Investigations

Thermal oxidative decomposition tests were conducted in a standard apparatus as described in reference 10. It consists of a 60 mm-long pyrex tube having a 15-mm lower part (12-mm ID) and a 45-mm upper part (22-mm ID).

A weighed amount of fluid (≈ 2 g) was placed in the lower part of the decomposition apparatus. The system was evacuated and backfilled with a known amount of oxygen (either 2.7×10^4 or 5.3×10^4 Pa at 25°C). The apparatus was then placed in a preheated furnace held at temperatures of 343 or $371^{\circ}\text{C} \pm 0.3^{\circ}\text{C}$. At test completion (≈ 24 hrs), the tube was removed from the furnace, allowed to cool to room temperature, attached to a vacuum line and the liquid nitrogen condensibles were trapped and weighed. A decomposition rate was then calculated as the number of milligrams of condensibles per gram of fluid per 24 hr. Test repeatability is typically, ± 10 percent (10).

In some tests, the residual fluid was left in the tube, additional oxygen was added and the test was continued by placing it back in the furnace. Test results appear in table 8 and figures 3(a) (343 °C) and (b) (371 °C). Test continuations are indicated by a superscript b in the table. Data for three lots of a commercial Fomblin Z-25 fluid are included for comparison.

Thermal-Oxidation-Corrosion Investigation

The same apparatus was used for the oxidation-corrosion tests. Metal coupons (M-50 steel, Ti, Ti4Al4Mn, Cu, and Ni) 19 mm O.D., 6.4 mm I.D., and 0.76 mm thick were polished with 600 grit sandpaper, rinsed with trichlorotrifluoroethane in an ultrasonic bath, then dried with compressed air. The coupons were weighed and positioned on a 6.4-mm glass rod with polytetrafluoroethylene spacers. The glass rod/coupon assembly was then placed in the bottom of the 22-mm I.D. glass tube and 20 ml of test fluid added. The tube was evacuated for approximately 30 min and then backfilled with either 5.3×10^4 Pa of oxygen or nitrogen (25 °C). The tube was then placed in a preheated furnace at 219 °C for 72 hr. The poly(methylene oxide) fluid was tested at two lower temperatures (177 °C (O₂) and 204 °C (N₂)). At test conclusion, the tube was removed from the furnace and allowed to cool to room temperature. The coupons were rinsed with trichlorotrifluoroethane for 2 min in an ultrasonic bath, dried for 5 min in air at 80 °C and weighed. The test fluid was filtered and kinematic viscosities were measured at 40 and 80 °C. Results for all fluids appear in table 9. Fluid weight loss was not determined.

Bulk Modulus

Isothermal secant bulk moduli were determined by compressing the fluids to 3.4×10^7 Pa (5000 psi) over a temperature range of 38 to 204 °C (100 to 400 °F). The apparatus was calibrated with distilled water. Results are compiled in table 10 for measurements at 2.07×10^7 Pa (3000 psi) and 38 °C and also appear in figure 4. Results for perfluoropolytrioxocane-I at various pressures and temperatures appear in table 11.

Stability in the Presence of AlCl₃

Fluid stabilities in contact with the Lewis acid, AlCl₃, were determined at temperatures from 50 to 160 °C. Approximately 20 g of fluid were placed in a 25-ml flask along with 2 g of freshly sublimed AlCl₃. An air-cooled condenser was placed on top of the flask. The flask, which was kept under a nitrogen atmosphere, was placed in a constant temperature bath for 24 hr. Following the test, the contents of the flask were weighed and a percent weight loss was calculated. Results are summarized in table 12, which include three commercial fluids (Fomblin Z-25, Demnum S-100, and Krytox 143AD) and three other fluids synthesized for other programs (perfluoroheptaglyme, perfluoropoly-tetrahydrofuran (F-THF), and perfluoropolydipropyleneglycol/formaldehyde (F-DPG/CH₂O)). These data also appear in figures 5(a) (100 °C), (b) (130 °C), and (c) (160 °C).

Lubrication Tests

The lubricating ability of the four synthesized fluids was measured using a four ball wear tester. Each fluid was tested under standard conditions (ASTM D 4172 B (i.e., 75 °C, 40-kg load, at 1200 rpm for 1 hr). Steel (52100) test specimens were used. Wear results for a single set of tests are tabulated in

table 13 and appear in figure 6 as a function of carbon to oxygen ratio. Repeat tests were precluded due to the volume of lubricant required for this test.

DISCUSSION

Thermal-Oxidative Stability

Three different sets of samples were tested. The first set included three fluids which were prepared by the early fluorination procedure (A): (DIOX-I), (TRIOX-I), and (TRIOX-II). The second set of fluids was prepared by the new fluorination procedure (B) and included (PEO), (DIOX-II), and (TRIOX-III). The final set was composed of three different lots of a commercially available Fomblin Z-25 fluid: lots P-21, P-28, and P-51.

Early Fluorination Procedure (A)

Oxidative degradation data for these fluids appear in table 8. Differences in data greater than the ± 10 percent test repeatability are considered significant. As indicated, tests 1 and 4 at 343°C for DIOX-I and TRIOX-I yielded high initial degradation rates, 122 and 65.1 mg/g/day, respectively. In addition, both fluids exhibited lower rates in test continuations re-using the residual fluid. (Tests 2 and 3 for DIOX-I and 5 to 7 for TRIOX-I.) This behavior is indicative of the presence of unstable species in the fluids which are subsequently removed during the test, resulting in a more stable residual fluid. These unstable species are probably related to the fluorination procedure (A) and may manifest themselves in the form of residual hydrogens or branch sites in the chain. The third fluid prepared by the early procedure (A) was TRIOX-II. It yielded less degradation than TRIOX-I (65.1 compared to 25.6 mg/g/day). TRIOX-II also showed less degradation in a subsequent test (20.5 mg/g/day) but not in third test continuation (23.7 mg/g/day). It is not clear why TRIOX-II was more stable than TRIOX-I, since both were produced by the same fluorination procedure.

Commercial Fomblin Z-25 Fluids

Data for the three lots of Fomblin Z-25 also appear in table 8 and figure 3(a) at 343 °C. All three lots had behavior similar to DIOX-I and TRIOX-I, in that subsequent tests on the same sample yielded lower decomposition rates. Lot P-21 (average 41.8 mg/g/day) was the least stable while lot P-51 (19.5 mg/g/day) yielded the lowest decomposition rate. All three Z-25 fluids yielded less degradation than DIOX-I and TRIOX-I. However, comparing test continuations for DIOX-I and TRIOX-I and all tests for TRIOX-II with the Z-25 lots indicates similar degradation rates.

New Fluorination Procedure (B)

343 °C Tests

A new fluorination procedure (B) was used to produce three additional fluids: PEO, DIOX-II, and TRIOX-III. This procedure was designed to produce a more linear fluid having less branched impurities. Indeed, the PEO fluid tested at 343 °C with twice the pressure of oxygen (test 20) yielded the lowest degradation rate (17.2 mg/g/day) for an initial test. However, even with this new procedure, a subsequent

test (21) with the PEO yielded a 50-percent improvement in oxidative stability to a low value of only 7.7 mg/g/day.

371°C Tests

Because of the lower degradation rates for fluids made with the new procedure (B), the test severity was increased from 343°C to 371°C and twice the pressure of oxygen was used. Results for these tests also appear in table 8 and figure 3(b). DIOX-II and TRIOX-III yielded lower initial results than Z-25-P-21 and both showed large improvements on test continuations. The PEO fluid yielded excellent results which were lower than either DIOX-II or TRIOX-III.

Residual Hydrogen

It was felt that the new fluorination procedure (B) might be producing more stable fluids by reducing the amount of residual hydrogen (below the detectability of proton NMR or infrared spectroscopy) left in the fluids. Therefore, one test (23) was performed on the DIOX-I fluid which had been prepared by the early fluorination procedure (A). This fluid was subjected to further fluorination at 275 °C for 12 hr which should further reduce the concentration of residual hydrogen. As seen in table 8, it still yielded higher degradation rates than DIOX-II (140 compared to 107 mg/g/day). Therefore, the presence of branch sites are considered to be more deleterious to oxidative stability than low levels (<5 ppm) of residual hydrogen in this particular test.

NMR Structure Determination

Although time limitations did not allow a series of test comparisons at 371°C between DIOX-II, TRIOX-III, PEO and the Z-25 lots, it is apparent that the former fluids, in particular, the PEO fluid is more stable towards oxidative degradation than Z-25 P21. In addition, there was an obvious difference between the various Z-25 lots themselves. Therefore, a ^{19}F NMR study was performed to determine the structural differences between the various Z-25 lots. The ^{19}F NMR results for these lots appear in table 14. Average compositions calculated from this table appear in table 15.

As indicated in table 15, the Z-25 fluid which was the most stable (P-51) contains the lowest concentration of formal ($-\text{OCF}_2\text{O}-$) (49.7% mol) while the least stable lot (P-21) contains the most (62.4% mol).

Small differences in the ($-\text{OCF}_2\text{O}-$) and ($-\text{OCF}_2\text{CF}_2\text{O}-$) ratio result in significant changes in fluid stability for Fomblin Z-25 because of the random nature of the structure. An increase in ($-\text{OCF}_2\text{O}-$) content of only a few percent increases the ^{19}F NMR resonance at 56.5 ppm ($-\text{OCF}_2\text{OCF}_2\text{OCF}_2\text{O}-$) markedly and to a lesser extent the resonance at 55.0 ppm ($-\text{OCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_2\text{O}-$). These two structures clearly appear to be weak links in Z fluids with ($-\text{OCF}_2\text{OCF}_2\text{OCF}_2\text{O}-$) representing the least oxidatively stable of the two. The concentration of this structure in Z-25 P-21 is more than twice that in P-51. As a result, P-21 decomposes at a rate more than twice that of P-51 at 343°C in an oxygen atmosphere (table 8) (average of 41.8 compared to 19.5 mg/g/day).

Oxidation-Corrosion Behavior

Oxidation-Corrosion results are summarized in table 9. Viscosity changes of less than 10 percent with coupon weight changes of less than 0.2 mg/cm^2 are not considered significant. Therefore, with respect to viscosity, all fluids were within this ± 10 percent change. Only two fluids yielded coupon weight changes greater than 0.2 mg/cm^2 . These were the PMO at 177°C in O_2 and TRIOX-II at 219°C in O_2 . However, there was no indication of serious oxidative degradation problems with any of these fluids under these conditions. However, it is clear that TRIOX-II yielded smaller viscosity changes than TRIOX-I.

Bulk Modulus

As expected, all fluids tested were very compressible and yielded comparatively low bulk modulus values (compared to a conventional silicate ester fluid, fig. 4). This is due to the low internal cohesive forces which give the PFPAE's many of their unique properties, such as low surface tension. As the carbon-to-oxygen ratio increased, a decrease in the bulk modulus was observed. For example, the PEO fluid having the least amount of oxygen ($\text{C/O} = 2$), exhibited the lowest bulk modulus (0.78 GPa) while the PMO fluid ($\text{C/O} = 1$) was the least compressible (i.e., highest bulk moduli). Based on these results, we conclude that covalently bonded oxygen in fluorocarbon ethers increases the bulk modulus; however, there are exceptions. Fluorocarbon fluids, such as perfluorokerosene, which do not contain oxygen, give bulk moduli values which are comparable to or exceed those of the PFPAE's (table 10 and fig. 4).

Stability in the Presence of AlCl_3

This study supports the theory that difluoroformal units ($-\text{OCF}_2\text{O}-$) in a polymer represent weak points which are susceptible to attack by Lewis acids (15 and 23). However, there is evidence that isolated formal units are more stable than adjacent units. In fact, isolated formal units have a Lewis acid stability comparable to that of tetrafluoroethylene oxide (PTO) units. For example, weight losses of 2.2, 7.1, 8.9, 100, and 100 percent, respectively, were obtained for PEO, TRIOX-II, DIOX-I, Z-25, and PMO at 130°C . F-trioxocane and F-dioxolane fluids with isolated formal units showed nominal weight loss as did the PEO, while Z-25, a fluid which contains some sequential formal units, decomposed completely. PMO, a fluid which contains ~ 95 percent formal units, decomposed violently, even at 100°C .

In addition, very stable formal-containing polymers can be prepared. For example, a perfluorinated 1:1 copolymer of dipropylene glycol and formaldehyde, designated as F-DPG/ CH_2O in table 12, is considerably more stable than PEO—a fluid which does not contain any formal units.

There is also a correlation between the carbon to oxygen ratio (in the backbone) and Lewis acid stability. For example, PEO (2:1 C/O ratio), Demnum S-100 (3:1 ratio) and perfluoropoly(tetramethylene oxide) (4:1), designated as Poly THF in table 12, have markedly different reactivities with AlCl_3 at 160°C . PEO decomposes completely, S-100 lost 9.5 percent of its weight while Poly THF lost only 3.2 percent. Weight loss at 130°C as a function of C/O ratio are shown in figure 7.

TRIOX-I gave unexpected results in this test and in the oxidation and oxidation/corrosion tests which do not correlate with the observations made with the other fluids. We suspect that this fluid was not perfluorinated and the anomalous behavior may be attributed to a higher than normal hydrogen content, but still not measurable by infrared or proton NMR ($< 5 \text{ ppm}$).

Lubrication Tests

Fluids having nearly identical molecular weights were selected for four-ball wear tests. Unfortunately, sufficient quantities of fluid were not available to run multiple tests and the results should therefore be viewed with caution. The preliminary observation is that as the carbon-to-oxygen ratio decreases so does the average wear scar. Data appear in table 13 and figure 6.

Density and Surface Tension

Density and surface tension for most fluids were measured by standard techniques and appear in the property tables 3 to 7. Both density and surface tension increased with decreasing carbon to oxygen ratio. These trends are illustrated in figures 8 and 9, respectively.

CONCLUSIONS

Several high molecular weight PFPAE fluids of varying structures were synthesized by direct fluorination. These fluids were characterized and subjected to a series of standard lubricant property tests. The following conclusions may be drawn:

1. As the carbon-to-oxygen ratio in the polymer repeating unit decreases: (1) the viscosity-temperature characteristics improve, (2) the bulk modulus increases (compressibility decreases), (3) surface tension increases, (4) density increases, and (5) the boundary lubricating properties may deteriorate.
2. The presence of difluoromethylene oxide (formal) units ($-\text{OCF}_2\text{O}-$) in the polymers do not significantly degrade oxidation and oxidation-corrosion stabilities as long as they are not sequential in the chain.

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TABLE 1.—NAMES AND PRIMARY CHEMICAL STRUCTURES
OF SYNTHESIZED PFPAE FLUIDS

Perfluoropoly-	Structure
(methylene oxide) (PMO)	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_x\text{CF}_3$
(ethylene oxide) (PEO)	$\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_x\text{CF}_3$
(dioxolane) (DIOX)	$\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{OCF}_2\text{O})_x\text{CF}_3$
(trioxocane) (TRIOX)	$\text{CF}_3\text{O}[(\text{CF}_2\text{CF}_2\text{O})_2\text{CF}_2\text{O}]_x\text{CF}_3$

TABLE 2.—NAMES AND PRIMARY CHEMICAL
STRUCTURES OF COMMERCIAL
PFPAE FLUIDS

Name	Structure
Demnum	$\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_x\text{C}_2\text{F}_5$
Krytox	$\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_x\text{C}_2\text{F}_5$
Fomblin Z	$\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_x(\text{CF}_2\text{O})_y\text{CF}_3$

TABLE 3.—PERFLUOROPOLYDIOXOLANE-I FRACTIONS AND PROPERTIES

Property		Fraction				
Kinematic viscosity (mm ² /sec)	Temperature, °C	101	102	103	104	105
	-40	23.2	125	646	2660	12 900
	20	2.83	7.92	23.0	50.8	238
	40	1.88	4.78	12.5	26.4	113
	60	1.33	3.14	7.68	15.5	63.0
	80	0.99	2.18	5.13	10.0	39.3
	95	0.81	1.69	3.78	8.11	30.3
	149	0.46	0.87	1.79	3.61	13.0
ASTM slope (ASTM D341)		0.901	0.758	0.604	0.527	0.417
Pour point (°C)		-107	-96	-87	-73	-66
Density (20 °C, g/ml)		1.768	1.801	1.830	1.845	1.855
Surface tension (dyne/cm)		15.7	16.9	19.0	18.9	18.3

TABLE 4.—PERFLUOROPOLYTRIOXOCANE-I FRACTIONS AND PROPERTIES

Property		Fraction				
Kinematic viscosity (mm ² sec)	Temperature, °C	201	202	203	204	205
	-40	33.9	382	2750	11 500	84 100
	20	3.04	10.7	37.4	105	502
	40	1.94	5.90	12.7	46.0	210
	60	1.36	3.67	10.0	24.5	105
	80	1.01	2.49	6.30	14.7	59.7
	95	0.84	1.98	4.85	11.2	45.3
	149	0.43	0.96	2.11	4.45	17.3
ASTM slope (ASTM D341)		0.945	0.769	0.648	0.560	0.440
Pour point (°C)		-100	-83	-70	-65	-55
Density (20 °C, g/ml)		1.766	1.806	1.832	1.848	1.858
Surface tension (dyne/cm)		15.4	16.8	18.2	18.6	18.6

TABLE 5.—PERFLUOROPOLYTRIOXOCANE-II FRACTIONS AND PROPERTIES

Property		Fraction				
Kinematic viscosity (mm ² /sec)	Temperature, °C	301	302	303	304	305
	-40	33.6	382	2550	7480	36 900
	20	3.22	11.8	38.9	83.3	291
	40	2.06	6.56	19.2	38.3	125
	60	1.44	4.13	11.1	21.1	65.7
	80	1.07	2.84	7.08	13.1	39.6
	95	0.88	2.24	---	10.1	29.7
	149	0.48	1.15	---	4.17	11.9
ASTM slope (ASTM D341)		0.901	0.725	0.615	0.549	0.451
Pour point (°C)		-100	-83	-70	-65	-55
Density (20 °C, g/ml)		1.765	1.808	1.829	1.849	1.857

TABLE 6.—PERFLUOROPOLY(METHYLENE OXIDE) FRACTIONS AND PROPERTIES

Property		Fraction				
Kinematic viscosity (mm ² /sec)	Temperature, °C	401	402	403	404	405
	-40	9.01	27.6	54.5	128	305
	20	2.18	4.89	8.78	18.4	41.3
	40	1.49	3.38	5.99	12.3	27.1
	60	1.12	2.49	4.32	8.81	19.1
	80	0.88	1.91	3.24	6.60	14.1
	95	0.72	1.55	2.59	5.25	11.0
	149	0.46	0.94	1.55	2.97	6.29
ASTM slope (ASTM D341)		0.837	0.629	0.523	0.418	0.352
Pour point (°C)		-120	-120	-119	-118	-115
Density (20 °C, g/ml)		1.794	1.822	1.840	1.846	1.852
Surface tension (dyne/cm)		16.4	17.9	20.1	19.8	18.3

TABLE 7.—PERFLUOROPOLY(ETHYLENE OXIDE) FRACTIONS AND PROPERTIES

Property		Fraction				
Kinematic viscosity (mm ² /sec)	Temperature, °C	501	502	503	504	505
	20	3.32	13.2	33.9	127	447
	40	2.07	7.21	16.1	51.9	173
	60	1.43	4.25	9.05	26.7	82.9
	80	1.05	2.80	5.73	15.5	44.9
	95	0.85	2.09	4.19	11.1	---
	149	0.46	1.07	1.93	4.27	11.4
ASTM slope (ASTM D341)		0.934	0.725	0.681	0.538	0.488
Pour point (°C) ^a		---	---	---	---	---
Density (20 °C, g/ml)		1.748	1.765	1.788	1.813	1.823

^aPerfluoropoly(ethylene oxide) has a melting point between 0 and 20 °C depending upon the average molecular weight of the sample.

TABLE 8.—THERMO-OXIDATIVE STABILITY OF
SEVERAL PERFLUOROPOLYALKYLETERS

Test number	Fluid	Fluorination procedure	Temperature, °C	Rate of condensable product formation, mg/g/day
^a 1	Diox-I	A	343	122
2	Diox-I ^b	A		59.6
3	Diox-I ^b	A		48.7
4	Triox-I	A		65.1
5	Triox-I ^b	A		53.4
6	Triox-I ^b	A		40.9
7	Triox-I ^b	A		29.2
8	Triox-II	A		25.6
9	Triox-II ^b	A		20.5
10	Triox-II ^b	A		23.7
11	Z-25 P-28 ^c	NA ^f		37.0
12	Z-25 P-28 ^b	NA ^f		21.3
13	Z-25 P-51	NA ^f		19.5
14	Z-25 P-51 ^b	NA ^f		13.7
15	Z-25 P-21	NA ^f		38.6
16	Z-25 P-21 ^b	NA ^f		29.9
17	Z-25 P-21	NA ^f		45
18	Z-25 P-21 ^b	NA ^f		33
19	Z-25 P-21 ^b	NA ^f	371	145
^d 20	PEO	B	343	17.2
21	PEO ^b	B	343	7.7
22	PEO ^b	B	371	21.4
23	Diox-I ^e	A		140
24	Diox-I ^b	A		83.2
25	Diox-II	B		107
26	Diox-II ^b	B		55.5
27	Triox-III	B		80.0
28	Triox-III ^b	B		29.6

^a2.7×10⁴ Pa oxygen used in tests 1 to 19. ^d5.3×10⁴ Pa oxygen used in tests 20 to 28.

^bFluid from previous test.

^eFluid refluorinated at 275 °C for 12 hr.

^cCommercial Fomblin Z-25 fluid.

^fNot Applicable

TABLE 9.—THERMAL-OXIDATION-CORROSION PROPERTIES OF SEVERAL PERFLUOROPOLYALKYLETERS

[5.3×10⁴ Pa gas pressure, 72 hr.]

Fluid	Temperature, °C	Atmosphere	Δ viscosity		Metal Weight Change, mg/cm ²				
			40 °C, percent	80 °C, percent	M-50 Steel	Ti	Ti4Al4Mn	Cu	Ni
DIOX-I	219	N ₂	+5.9	+6.7	-0.03	+0.13	+0.13	-0.06	+0.03
	219	O ₂	+4.4	+5.5	-.03	-.06	-.03	+.03	-.10
PEO	219	N ₂	0	-0.3	+.03	-0.03	0	-0.03	0
	219	O ₂	0	-.7	+.12	+.06	+.09	+.09	0
TRIOX-I	219	N ₂	+4.8	+3.3	0	+0.06	+0.13	-0.03	+0.06
	219	O ₂	+8.2	+3.3	+.09	+.06	+.06	+.18	+.06
TRIOX-II	219	N ₂	+1.6	+1.4	0	0	+0.06	-0.06	-0.06
	219	O ₂	+1.5	+1.1	+.16	+.16	+.09	^b -.22	0
PMO	204	N ₂	(a)	(a)	-0.16	+0.16	+0.16	-0.09	-0.09
	177	O ₂	(a)	(a)	^b +.51	+.16	+.16	-.03	+.16

^aNot measured.

^bGreater than 0.2 mg/cm².

TABLE 10.—BULK MODULUS FOR SEVERAL
PERFLUORINATED FLUIDS

[2.07×10^7 Pa (3000 psi), 38 °C.]

Fluid	GPa	psi
Perfluoropoly(ethylene oxide) (Fraction 502)	0.78	113 000
Perfluoropolytrioxocane-II (Fraction 302)	0.81	118 000
Perfluoropolydioxolane-I (Fraction 102)	0.85	123 000
Perfluoropoly(methylene oxide) (Fraction 402)	0.89	129 000
Perfluorokerosene ^a	0.91	132 000

^aNonoxygen containing fluorocarbon.

TABLE 11.—ISOTHERMAL SECANT BULK MODULI FOR PERFLUOROPOLYTRIOXOCANE-I
(FRACTION 203) AT VARIOUS PRESSURES AND TEMPERATURES

Bulk Modulus GPa (psi)						
Temperature, °C	Pressure Pa (psi)					
	6.9×10^6 (1000)	1.4×10^7 (2000)	2.1×10^7 (3000)	2.8×10^7 (4000)	3.5×10^7 (5000)	
38	0.82 (119 000)	0.84 (122 000)	0.88 (127 000)	0.90 (130 000)	0.92 (133 000)	
66	0.70 (102 000)	0.70 (101 000)	0.71 (103 000)	0.72 (104 000)	0.73 (106 000)	
93	0.49 (71 000)	0.52 (75 000)	0.54 (78 000)	0.55 (80 000)	0.57 (83 000)	
121	0.41 (59 000)	0.42 (61 000)	0.45 (65 000)	0.48 (69 000)	0.48 (69 000)	

TABLE 12.—STABILITY OF VARIOUS PERFLUOROPOLYALKYLETERS IN THE PRESENCE
OF $AlCl_3$ (24-HR TEST)

Weight loss, percent					
Fluid	C/O ratio	Temperature, °C			
		50	100	130	160
Perfluoroheptaglyme ^a	2:1	---	2.0	5.0	---
TRIOX-I (Fraction 202)	5:3	---	2.5	100	---
TRIOX-II (Fraction 302)	5:3	---	1.3	7.1	20
PEO (Fraction 502)	2:1	---	1.4	2.2	100
DIOX-I (Fraction 102)	3:2	---	1.8	8.9	100
PMO (Fraction 402)	1:1	20	100	100	---
Fomblin Z-25	~1.4:1	2.6	36	100	100
Demnum-S100	3:1	---	1.2	1.6	9.5
Krytox-143	3:1	---	1.8	---	5.7
Perfluorinated poly THF ^b	4:1	---	---	---	3.2
Perfluorinated poly DPG/ CH_2O ^c	7:3	---	---	---	9.7

^a $CF_3O(CF_2CF_2O)_7CF_3$

^b $CF_3O(CF_2CF_2CF_2CF_2O)_nCF_3$

^c $CF_3O\{[CF(CF_3)CF_2O]_2CF_2O\}_nCF_3$

TABLE 13.—FOUR BALL WEAR DATA FOR SEVERAL
PERFLUOROPOLYALKYLETERS IN AIR

[75 °C, 40 kg, 1200 rpm, 60 min, 52100 steel specimens.]

Fluid	Nominal C/O ratio	Average wear scar, mm
PEO (Fraction 503)	2	0.52
TRIOX-II (Fraction 303)	1.67	0.65
DIOX-I (Fraction 103)	1.5	0.69
PMO (Fraction 403)	1.0	1.82

Table 14.—¹⁹F NMR RESULTS FOR THREE LOTS OF FOMBLIN Z-25

Structure	δ ppm	Relative intensity, percent		
		P-51	P-21	P-28
$\text{OCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_2\text{CF}_2\text{O}$	53.2	9.7	6.8	7.3
$\text{OCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_2\text{O}$	55.0	15.7	20.5	19.4
$\text{OCF}_2\text{OCF}_2\text{OCF}_2$	56.5	6.5	16.4	14.6
$\text{CF}_3\text{OCF}_2\text{CF}_2\text{O}$	57.3	0.5	0.7	0.5
$\text{CF}_3\text{OCF}_2\text{O}$	59.2	0.5	0.7	0.5
$\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}$	82.7	1.6	1.4	1.0
$\text{OCF}_2\text{CF}_2\text{CF}_2\text{O}$	84.3	1.8	1.7	2.4
$\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{O}$	90.7	27.7	16.4	18.5
$\text{OCF}_2\text{OCF}_2\text{CF}_2\text{O}$	92.5	33.7	32.9	32.6
$\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}$	127.3	1.4	1.4	1.4
$\text{OCF}_2\text{CF}_2\text{CF}_2\text{O}$	131.2	0.9	1.0	1.0

TABLE 15: COMPOSITION OF VARIOUS LOTS OF Z-25
FLUIDS AS DETERMINED BY ¹⁹F NMR

Structure	Mol % in polymer chain		
	P-51 ^a	P-21 ^a	P-28 ^a
$-\text{OCF}_2\text{O}-$	49.7	62.4	60.2
$-\text{OCF}_2\text{CF}_2\text{O}-$	47.8	35.3	37.3
$-\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$	1.4	1.0	0.9
$-\text{OCF}_2\text{CF}_2\text{CF}_2\text{O}-$	1.2	1.3	1.6
Ratio $\text{OC}_2\text{F}_4\text{O}/\text{OCF}_2\text{O}$	0.96	0.57	0.62

^aLot number.

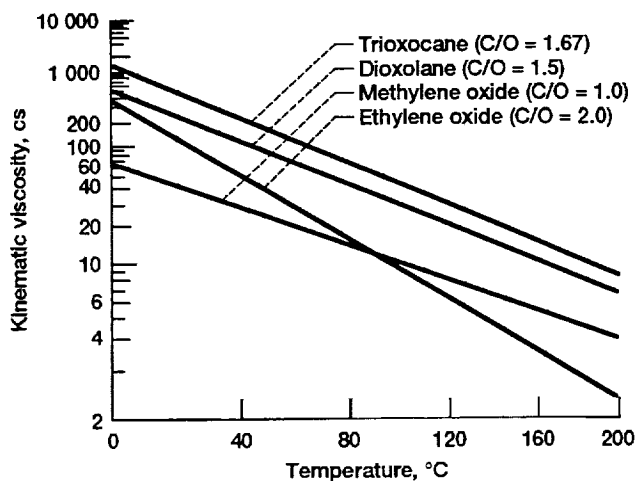


Figure 1.—Kinematic viscosity as a function of temperature for several PFPAE fluids (ASTM D-341).

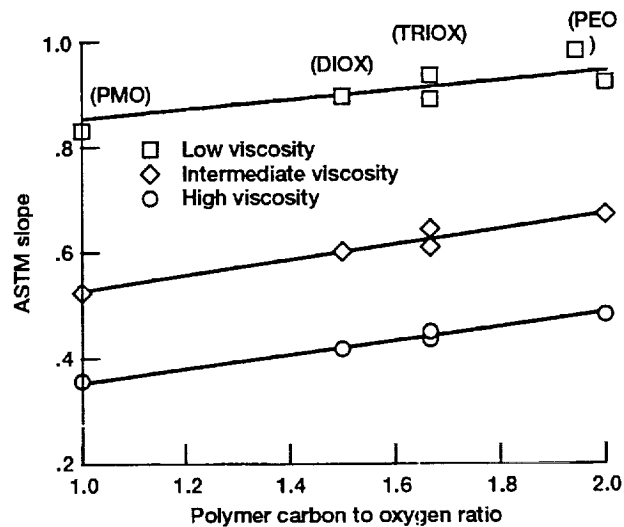


Figure 2.—ASTM slope (D-341) versus carbon to oxygen ratio for a series of PFPAE fluids.

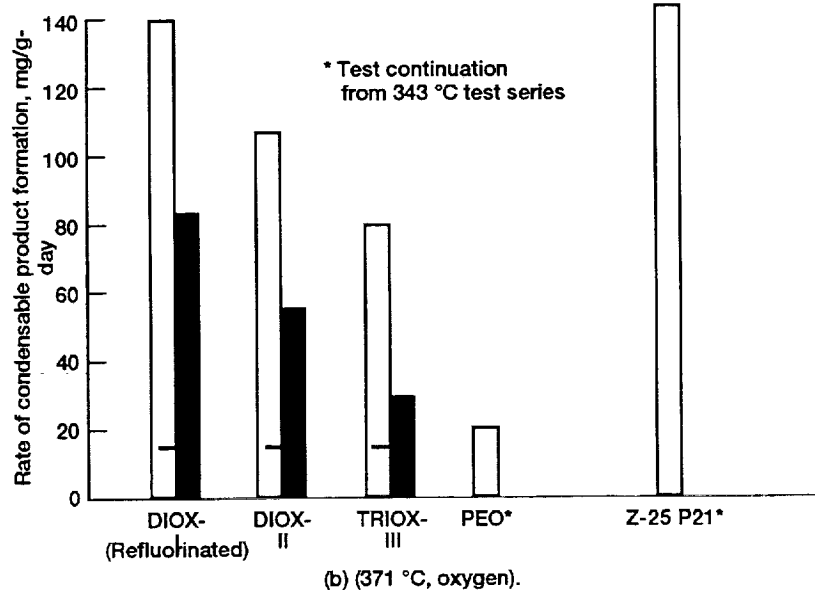
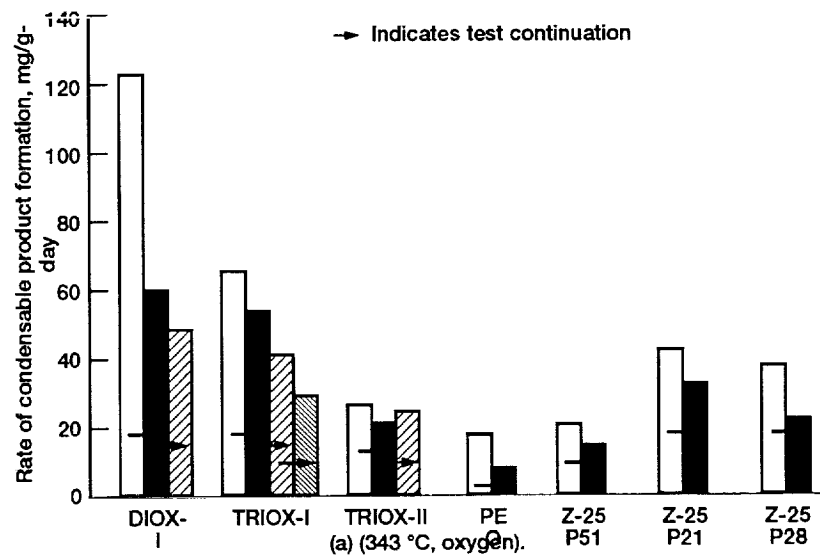


Figure 3.—Thermal-oxidative degradation of several PFPAE fluids.

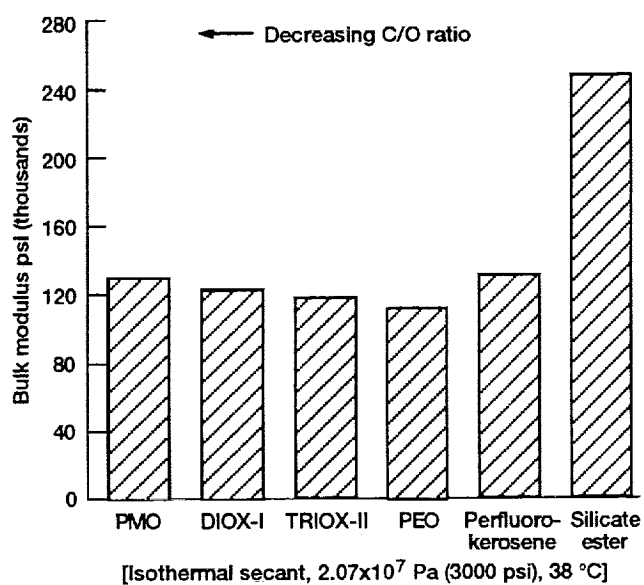


Figure 4.—Bulk modulus for a series of PFPAE fluids.

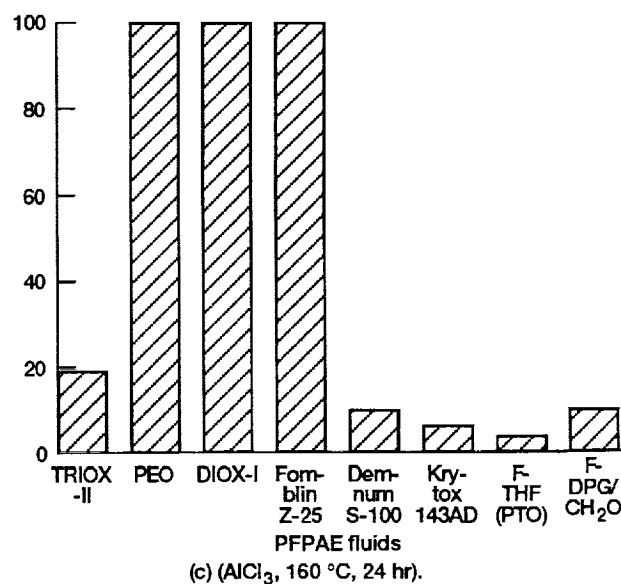
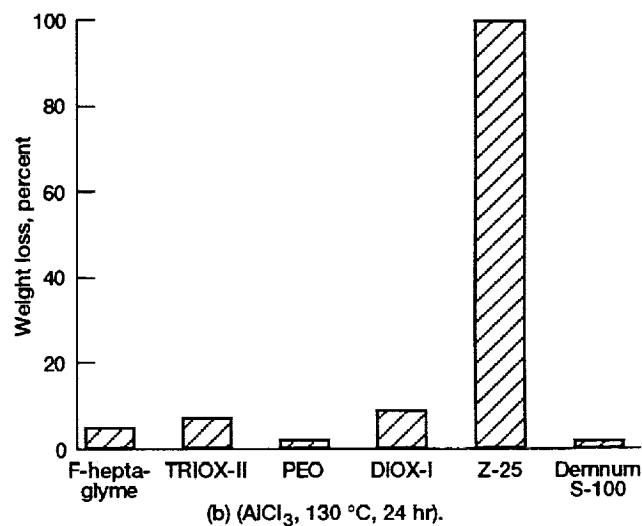
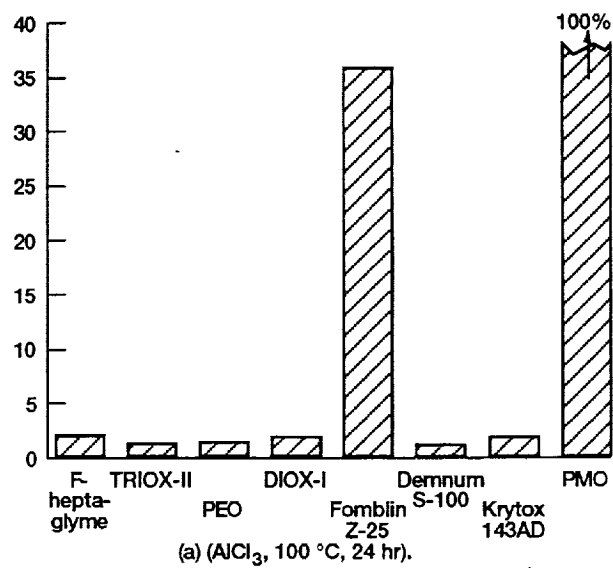


Figure 5.—Lewis acid stability for a series of PFPAE fluids.

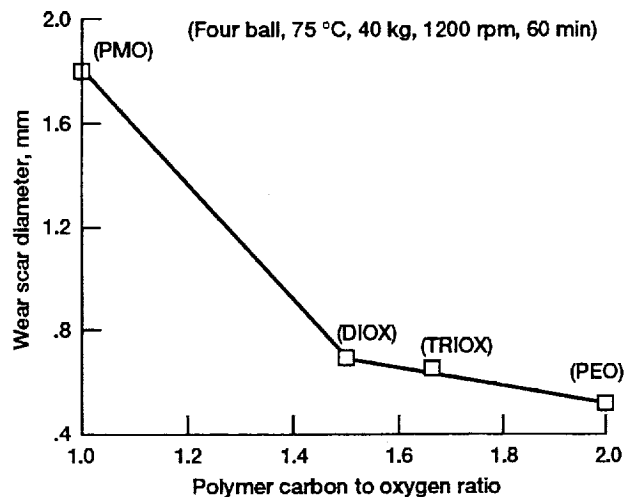


Figure 6.—Wear scar diameter versus carbon to oxygen ratio for a series of PFPAE fluids in air.

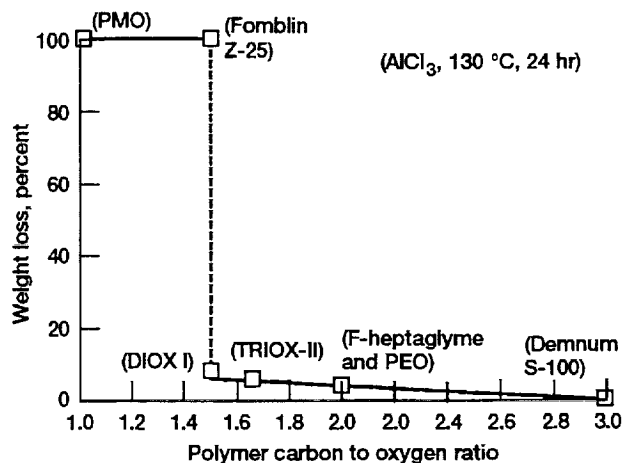


Figure 7.—Lewis acid stability versus carbon to oxygen ratio for a series of PFPAE fluids.

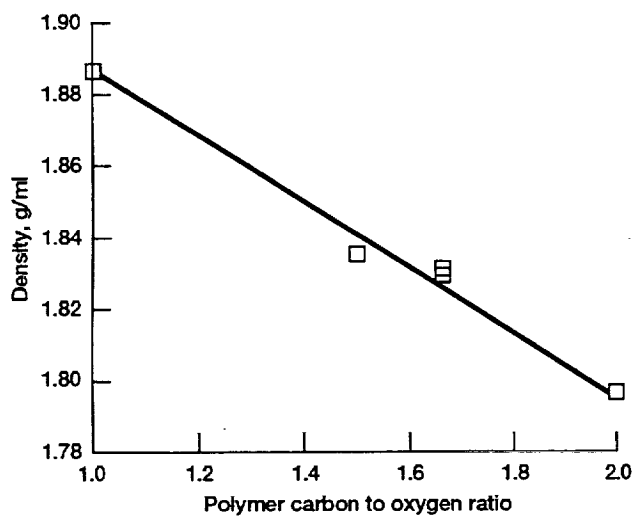


Figure 8.—Density versus carbon to oxygen ratio for a series of PFPAE fluids.

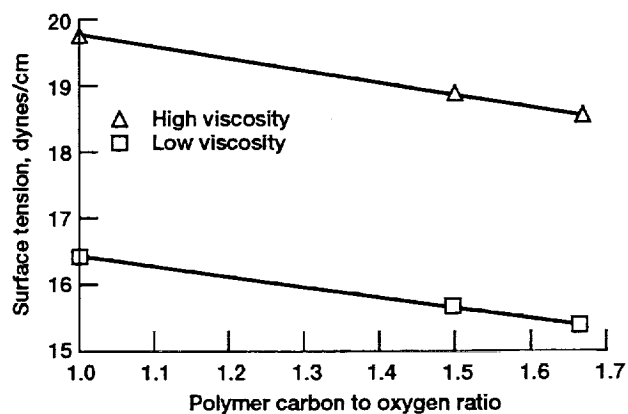


Figure 9.—Surface tension versus carbon to oxygen ratio for a series of PFPAE fluids.

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13. ABSTRACT (Maximum 200 words) A series of perfluoropolyalkylether (PFPAE) fluids was synthesized by direct fluorination. Viscosity-temperature properties, oxidation stabilities, oxidation-corrosion properties, bulk modulus, lubricity, surface tension and density were measured. It was shown that as the carbon to oxygen ratio in the polymer repeating unit decreases, the viscometric properties improve, the fluids may become poorer boundary lubricants, the bulk modulus increases, the surface tension increases and the fluid density increases. The presence of difluoromethylene oxide units in the polymer does not significantly lower the oxidation and oxidation-corrosion stabilities as long as the difluoromethylene oxide units are separated by other units.				
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